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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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SUISSE

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A process for the synthetic generation of methane

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Description

5

A process for the synthetic generation of methane

The invention relates to a process for the synthetic
generation of methane from a feed gas mixture comprising
10 carbon monoxide, hydrogen and water vapour and optionally
aromatic hydrocarbons.

It is the intention of the world-wide community to reduce the
production of gaseous climate relevant components, such as
15 chlorofluorocarbons (CFC) and carbon dioxide.For the carbon
dioxide the worldwide community committed itself to reduce the
production within the next decade in the range of about 10 to
15%, depending on the country and its commitment to the Kyoto
agreement.
20

So-called biofuels have the potential to influence the carbon
dioxide balance tremendously on a midterm and long-term basis
as being a relevant source for renewable primary products,
such as wood or related biomass. The estimated cost are
25 expected in the range of 300 Swiss Francs per ton of CO_2. These
costs are compared to other options taken in the
transportation sector quite inexpensive.

Beside natural gas (methane) and hydrogen the biofuels are
30 categorized as potential alternative. On a short-term fuels
like RME (bio diesel), ethyl alcohol and bio gas, are
available; in mid- to long-term, bio -fuels will be produced
according to the already theoretically well-known thermo-
chemical processes which take advantage of a catalyst in order
35 to transform a synthesis gas into the desired bio fuel, such
as methyl alcohol, synthetic gasoline or diesel, methane, or
hydrogen.

A most promising fuel is methane that is supplied actually as
fossil gas and which can be replaced under efficient use of
synergies between the required infrastructure for both the
5   fossil gas and the biogenic gas by the latter that can be
produced by fermentation as well as by thermo-chemical
processes.

Unfortunately, one of the most preferred renewable raw
10   material, wood, cannot be transformed into bio gas by
fermentation. Therefore, it is a crucial task to provide
efficient alternative processes for the synthetic generation
of methane from synthesis gas originating from wood
gasification processes.

15

A process known in the art uses wood in a gasification
reactor, such as FICFB (Fast Internally Circulation Fluidised
Bed), which requires subsequently non-negligible efforts for
the pretreatment of the raw synthesis gas in order to allow
20   both effective and efficient synthesis of methane. As far as
wood is considered as the renewable raw material, it has to be
pointed out that the raw synthesis gas originating from the
gasification step, is loaded with considerable amounts of
aromatic hydrocarbons which are known in the prior art to have
25   a negative impact in the subsequent process chain. Therefore,
the removal of these aromatic hydrocarbons, such as benzene,
toluene and naphthaline (BTN), is acknowledged as being a
required process requisite as well as the removal of ammonia
NH_3 and hydrogen sulfide H_2S. Unfortunately, these additional
30   process requisites tend to increase the cost of the synthetic
generation of methane from woodand reduce the overall
efficency.

For the reason given above, the crucial pre-requisite for an
35   efficient exploitation of wood for the synthetic generation of
methane is to find an optimized concert between the processes
of gasification, raw synthesis gas purification and methane

generation. Of central importance are the properties of the catalyst required for the generation of methane.

Accordingly, it is the aim of the invention to provide a
5   process which allows the synthetic generation of methane for a renewable raw material, explicitly including wood and related materials, in an economically and feasible manner.

This aim is achieved according to the invention by a process
10   for the synthetic generation of methane from a feed gas mixture, i.e. a feed gas mixture originating from a biomass gasification process, comprising carbon monoxide, hydrogen and water vapour and optionally aromatic hydrocarbons; said process comprising the steps of:

15   a) bringing the feed gas mixture in contact with a fluidized bed catalyst having catalyst particles which comprise as catalytic active component a metal and/or a metal compound or a mixture thereof;
under the circumstances of:

20   b) an elevated temperature in the range of 250 to 500°C;
         c) a feed gas pressure in the range of 0.8 to 70 bar;
         d) a gas hourly space velocity of 1000 to 50000 h^{-1}; and
         e) a concentration of H_2/CO in the feed gas mixture in the range of 0.25 to 5.

25

The afore-mentioned process allows to catalytically convert hydrogen and carbon monoxide effectively in the fluidized bed. Using a fluidized bed catalytic reactor avoids a rapid deactivation of the catalyst material and therefore delivers a
30   high activity of the catalytic active components in the process.

Both thermo-chemical reactions, the endothermic reformation of higher hydrocarbons, i.e. aromatic hydrocarbons, and the

exothermic methane generation, proceed simulataneously within the fluidized bed catalytic reactor, leading to an overall enhanced thermal efficiency of the conversion process.

5   With respect to the initial and continuing catalytic activity, excellent results have been achieved by using as catalytically active component nickel and/or a nickel compound, preferably a mixture of nickel and nickel monoxide, deposited on an ceramic carrier, such as Al_2O_3, TiO_2, SiO_2 or Y_2O_3 or mixtures thereof.

10 Additionally, the content of the catalytically active component may be in the range of 20 to 80 weight%, preferably 40 to 60 weight%, as compared to the weight of the catalyst particles. A suitable catalyst may comprise nickel and nickel oxide deposited on alumina (Al_2O_3) having a content of the

15 catalytically active component in the range of 50 weight% as calculated as neat nickel.

In order to achieve both, a high mobility of the catalyst particles in the fluidized bed, and a sufficient reactive

20 surface area, the size of the catalyst particles may be in the range of 10 to 1000 µm, preferably in the range of 100 to 500 µm.

With respect to the energy balance of the exothermic

25 generation of methane an advantageous feed gas composition is considered to have a positive impact thereupon when the feed gas mixture comprises aromatic hydrocarbons, such as benzene, toluene and naphthalene, in the range of less than 10 Vol%, preferably less than 5 vol%. Explicitly, this gas composition

30 covers broadly a synthesis gas that originates from wood gasification processes to which a major focus is laid upon due to the environmental demands.

An optimal yield with respect to the generation of methane as
well as to a complete conversion of the higher hydrocarbons
may require that the gas hourly space velocity (GHSV) is in
the range of 2000 to 10000 h^{-1}, the temperature is in the range
5   of 340 to 400°C and the gas pressure is in the range of 0.8 to
10 bar. With respect to the above-mentioned nickel/nickel
oxide catalyst, the temperature may preferably be at about
350°C, and the GHSV at about 4200 h^{-1} .

10   In order to offer conditions in the fluidized bed catalyst
that support both the catalytic reactions of reforming higher
hydrocarbons and formation of methane and the regeneration of
the catalyst particles, a mean residence time of the feed gas
mixture in the fluidized bed catalyst may range from 0.1 to 5
15   sec., preferably 0.2 to 1 sec.

Again with respect to the yield of methane and to the
reformation of higher hydrocarbons the content of H_2/CO in the
feed gas mixture is in the range of 0.8 to 3, for example in
20   the range of 1.5 as combined with the afore-mentioned
nickel/nickel oxide catalyst.

Exemplarily embodiments of the inventive process are described
in detail below without the intention to limit the invention
25   to these actually preferred examples.

The measurements were taken with a plant as shown
schematically below in Figure 1. The measurement campaign can
be divided in three different sections:
30
Phase 1:   The feed gas mixture is pretreated with a wet
           scrubberunit and an activated carbon filter
           (charcoal absorber) as proposed so far in the prior
           art which teaches the process as being unactable

without prior gas cleaning and removal of aromatic
hydrocarbons;

Phase 2: The feed gas mixture is now only pretreated with the
         wet scrubber unit; charcoal absorber has been
         bypassed being aware of a possible catalyst
         deactivation reported so far in the prior art due to
         carbon which is deposited on the catalytic surfaces
         and by that blocks their reactivity (coking); and

Phase 3: The feed gas mixture is taken as of the outlet of
         the wood gasification plant without any pretreatment
         as disclosed in the prior art.

Especially for the intention of maintaining the activity and
selectivity of the catalyst, unsaturated hydrocarbons (such as
C_2H_4, C_2H_2), light tar components (such as benzene, toluene,
naphthaline, phenylacethylene, styrole, indene) and ammonia
are known according to the prior art as being highly
disturbing these demands.

Figure 1 shows that the complete plant comprises an inlet at
1) for the feed gas mixture originating from a non-illustrated
wood gasification plant, followed by a wet scrubber unit at
2), an activated carbon filter at 3), a gas pump and the
methane generation unit COALA whereby the methane content is
observed at the outlet of COALA at 4). The methane generation
unit COALA comprises a desulphurisation unit in form of a ZnO
fixed bed reactor, an inlet for the supply of water vapour, a
fluidized bed catalyst, a filter and a heat exchanger as seen
in direction of the gas flow.

In phase 1, the washer unit for the removal of ammonia NH_3 and
the activated carbon filter for the removal of higher
hydrocarbons are installed upstream the methane generation
unit COALA. The gas composition during the first 40 hours of
service is given in table 1; the first line giving the data

for the gas composition upstream the activated carbon filter, the second and third lines the respective gas compositions downstream the activated carbon filter after 3 and 40 h of service, resp.

5

Table 2 gives the gas compositions in phase 1 with respect to benzene, toluene, naphthaline and C8 at the probe locations 1), 2), 3) and 4). Almost all disturbing higher hydrocarbons are already removed at 3) by both the wet scrubber unit and

10   the activated carbon filter which is the desired effect of gas purification being declared as a pre-requisite in the prior art for the efficient subsequent methane generation. The plant was operated continuously at a temperature of about 360°C, a water content of 0.25 as related to the dry gas volume and a

15   gas volume flow rate of 0.6 m^3/h.

During phase 2, the plant was operated without activated carbon filter (bypassing line named Phase 2+3 in Fig. 1) and the gas composition with respect to higher hydrocarbons is

20   given in table 3. Surprisingly, a reduction of the content of higher hydrocarbons can be observed although the carbon filter unit has been bypassed.

During phase 3, the plant was operated without any

25   pretreatment of the feed gas mixture according to the present invention. As already before in phases 1 and 2, for the fluidized bed catalyst 100 g catalyst particles having a size of 200 μm and comprising an even content of nickel and nickel oxide supported by alumina (Al_2O_3) whereby the content of the

30   catalytically active nickel components is 50 weight% as calculated as neat nickel, was used. The gas composition for the higher hydrocarbons is given in table 4. At the entrance the average load of benzene, toluene, naphthaline and C8 was in the range of 13.6 g/Nm^3 resp. 0.6 g/Nm^3 resp. 0.8 g/Nm^3

35   resp. 0.5 g/Nm^3. At the outlet at 4) these higher hydrocarbons were reformed almost completely without the occurrence of any catalyst deactivation or loss in selectivity.

The comparison data given in table 5 is in so far self-explanatory, when the following definitions are observed:

5   The steam/dry gas ratio

$$D_V = \frac{n_{H2O}}{n_{Gas\,tr.}} \quad [-]$$

is the molar ratio of water steam to all the other gas
10   components. The catalyst load is expressed as the ratio of the number of moles of gas brought into contact with a given mass of catalyst per hour.

$$KB = \frac{n_{Gas\,tr} + n_{H2O}}{M_{Kat}} \quad \left[\frac{mol}{kg \cdot h}\right]$$

15

originating from the generation of methane from synthesis gas, such as pure H_2/CO gas. The „steam to carbon ratio"

$$S/C = \frac{n_{H2O}}{n_{Carbon}} \quad [-]$$

20

is the molar ratio of water steam to total amount of carbon in the gas and is known from the steam reforming of methane. All above mentioned key figures are used in a sense that clearly determined distinct gas compositions were used. Therefore,
25   they are not sufficient in order to describe the process of generating methane from a synthesis gas being achieved by a biomass gasification process. Additionally, the H/C ratio in both a dry product gas

30   $$H/C_{tr} = \frac{n_H}{n_C}$$

as well as in a humidified product gas

$$H/C_f = \frac{n_H + 2 \cdot n_{H2O}}{n_C}$$

is a suitable parameter to characterize the process properly. A further meaningful parameter is the conversion rate of carbon monoxide

$$U_{CO} = \frac{n_{COin} - n_{COout}}{n_{COin}} \quad [-],$$

the selectivity to methane

$$S_{CH4} = \frac{n_{CH4in} - n_{CH4out}}{(n_{COin} - n_{COout}) + x \cdot (n_{CxHyin} - n_{CxHyout})} \quad [-]$$

and the so called cold gas efficiency,

$$\eta_{KG} = \frac{Heatingvalue_{CH4out}}{Heatingvalue_{in}}$$

which describes the heating value of the methane at the outlet in relation to the overall heating value of the gas at the inlet.

Surprisingly, the catalyst does not show any effect of deactivation and/or loss in selectivity which is indicated by the data given in the third and forth line. The third line stands for the results in phase 3a during the initial hours of operation. The results in the forth line stand for the gas compositions that have been achieved by continuously operating the plant over dozends of hours.

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Patent Claims

1. A process for the synthetic generation of methane from a feed gas mixture comprising carbon monoxide, hydrogen and water vapour and optionally aromatic hydrocarbons; said process comprising the steps of:
   a) bringing the feed gas mixture in contact with a fluidized bed catalyst having catalyst particles which comprise as catalytic active component a metal and/or a metal compound or a mixture thereof under the circumstances of:
   b) an elevated temperature in the range of 250 to 500°C;
   c) a feed gas pressure in the range of 0.8 to 70 bar;
   d) an gas hourly space velocity of 1000 to 50000 h^{-1}; and
   e) an concentration of H_2/CO in the initial gas mixture in the range of 0.25 to 5.

2. The process according to claim 1,
characterized in that
the catalytic active component is nickel and/or a nickel compound, preferably a mixture of nickel and nickel oxide, disposed on an ceramic carrier, such as Al_2O_3, TiO_2, SiO_2 or Y_2O_3 or mixtures thereof.

3. The process according to claim 2,
characterized in that
the content of the catalytically active component is in the range of 20 to 80 weight%, preferably 40 to 60 weight%, as compared to the weight of the catalyst particles.

4. The process according to claim 1, 2 or 3,
characterized in that
the size of the catalyst particles is in the range of 10 to

5   1000 μm, preferably in the range of 100 to 500 μm.

5. The process according to anyone of the preceding claims,
characterized in that
the feed gas mixture comprises aromatic hydrocarbons, such as

10   benzene, toluene and naphthalene, in the range of less than 10
Vol%, preferably less than 5 vol%.

6. The process according to anyone of the preceding claims,
characterized in that

15   the gas hourly space velocity is in the range of 2000 to 10000
h^{-1}, the temperature is in the range of 340 to 400°C and the
gas pressure is in the range of 1 bar.

7. The process according to anyone of the preceding claims,

20   characterized in that
a mean residence time of the feed gas mixture in the fluidized
bed catalyst is in the range of 0.1 to 5 sec., preferably 0.2
to 1 sec.

25   8. The process according to anyone of the preceding claims,
characterized in that
the content of H_2/CO in the feed gas mixture is in the range of
0.8 to 2.

30

EPO - Munich
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25. März 2004

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Abstract

The present invention discloses a process for the synthetic
generation of methane from a feed gas mixture comprising
carbon monoxide, hydrogen and water vapour and optionally
aromatic hydrocarbons; said process comprising the steps of:

a) bringing the feed gas mixture in contact with a fluidized
bed catalyst having catalyst particles which comprise as
catalytic active component a metal and/or a metal
compound or a mixture thereof under the circumstances of:

b) an elevated temperature in the range of 250 to 500°C;

c) a feed gas pressure in the range of 0.8 to 70 bar;

d) a gas hourly space velocity of 1000 to 50000 h^{-1}; and

e) a concentration of H_2/CO in the initial gas mixture in the
range of 0.25 to 5.

The afore-mentioned process allows to catalytically convert
hydrogen and carbon monoxide effectively in a fluidized bed
catalytic reactor which avoids a rapid deactivation of the
catalyst material and therefore delivers a high activity of
the catalytic active components in the process. Both thermo-
chemical reactions, the endothermic reformation of higher
hydrocarbons, i.e. aromatic hydrocarbons, and the exothermic
methane generation, proceed simulataneously within the
fluidized bed catalytic reactor, leading to an overall
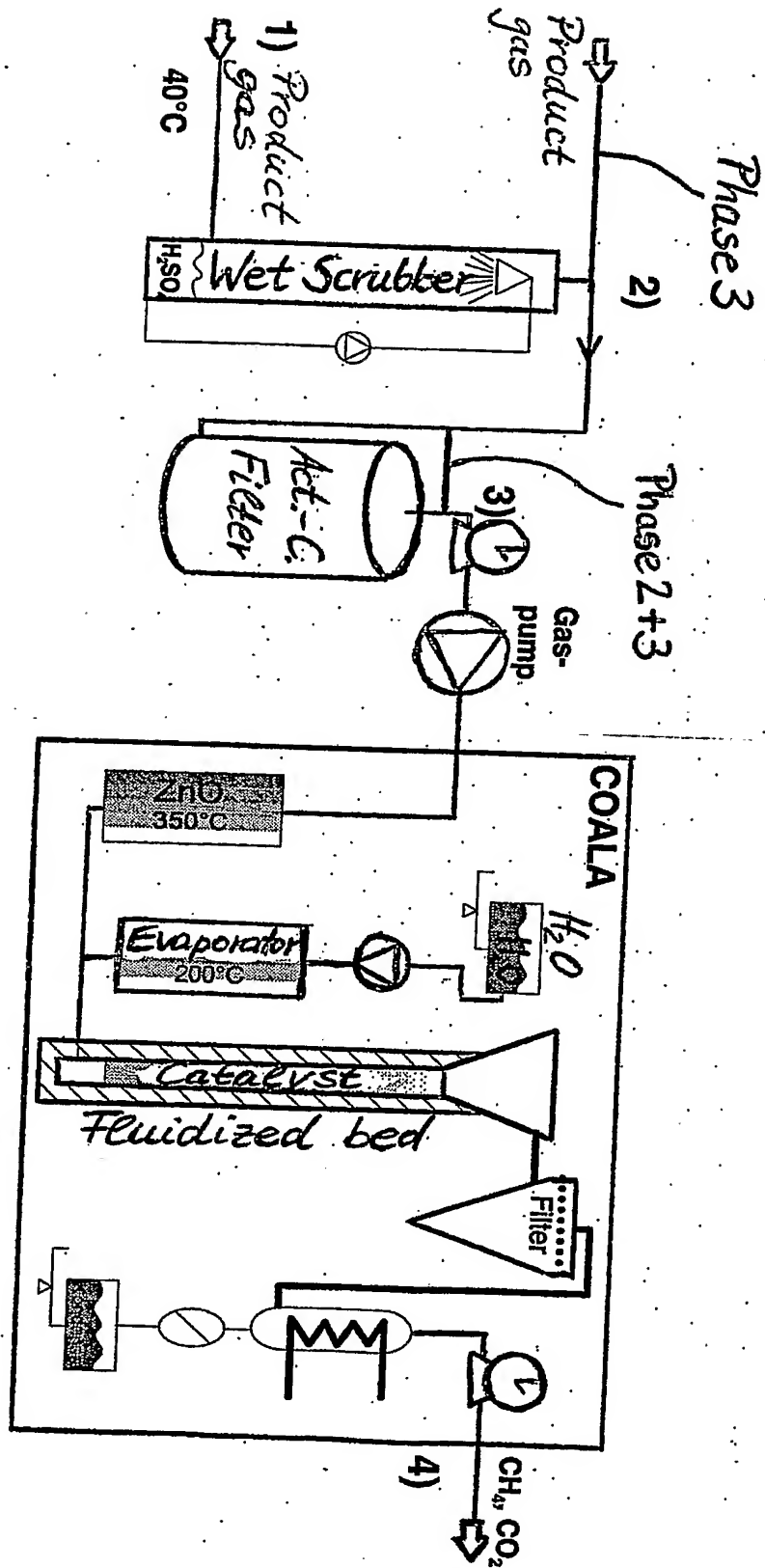enhanced thermal efficiency of the conversion process.

Fig. 1

Phase 1	CO2 %	C2H4 %	C2H6 %	C2H2 %	H2 %	O2 %	N2 %	CH4 %	CO %
Upstream Act.-C.	18.99	2.36	0.34	0	40.3	0.18	2.1	10.28	26.89
Downstream Act.-C. Filter (3h)	16.6	0.85	0.25	0	43.9	-	2.5	9.4	29.1
Downstream Act.-C. Filter (46h)	17.3	1.46	0.24	Erstmals Peak	41.0	0.092	2.16	10.8	28.9

Table 1

Phase 1	Benzene [mg/Nm³]	Toluene [mg/Nm³]	Naphthaline [mg/Nm³]	C8 [mg/Nm³]
Inlet at 1)	21440	1068	1411	814
Inlet at 1)	14813	726	839	573
Product gas, downstream wet scrubber at 2	7456	548	674	561
Inlet COALA, after wet scrubber & Act.-C. at 3	232	19	28	16
Outlet COALA 4)	5	0	3	0
Outlet COALA 4)	2	0	3	0

Table 2

Phase 2

	Benzene [mg/Nm³]	Toluene [mg/Nm³]	Naphthaline [mg/Nm³]	C8 [mg/Nm³]
Inlet COALA, after wet scrubber, without Act.-C.Filter	9658	373	234	263
Inlet COALA after wet scrubber, without Act.-C.Filter:	13953	531	448	485
Inlet at 1)	21440	1068	1411	814
Inlet at 1)	14813	726	839	573

Table 3

Phase 3

	Benzene [mg/Nm³]	Toluene [mg/Nm³]	Naphthaline [mg/Nm³]	C8 [mg/Nm³]
Inlet COALA, without any pre-treatment	17252	572	696	425
Inlet COALA, dito	13601	477	605	346
Inlet COALA, dito	11493	630	1013	670
Inlet COALA, dito	12152	571	723	510
Outlet COALA 4)	157	9	3	0
Outlet COALA 4)	136	9	1	0

Table 4

	V_{GAS} Nl/min	V_{FEED} ml/min	T_{Ruch} °C	D_v	KB	S/C	H/C_T	H/C_B	U_{CO}	U_{BTH}	S_{CH4}	n_{KG}
BILANZ1 Phase I	9.54	0.91	362.4	0.180	263.2	0.30	2.73	2.14	0.99	0.987	0.55	0.80
BILANZ2 Phase II	10.42	0.95	359.8	0.177	282.5	0.27	2.62	2.07	0.97	0.990	0.64	0.84
BILANZ3 Phase IIa	10.80	0.94	357.0	0.164	299.7	0.27	2.54	2.03	0.96	0.992	0.65	0.84
BILANZ4 Phase IIb	7.44	1.04	360.60	0.229	217.6	0.35	2.72	2.03	0.98	0.992	0.64	0.85

Table 5